

Charge Addition Effects in Phenylene Ethynylene Oligomers: The Effect of -NO₂ Substitution

Interest in aromatic systems based on phenylene ethynylene oligomers (OPE) has been driven by reports of negative differential resistance/hysteretic behavior, analogous to switching, in metal-molecule-metal junctions. Theoretical work has invoked the importance of charge addition effects on conformation and electronic structure and polaronic effects to provide potential explanations for this behavior. Understanding the effect of charge addition in these aromatic molecular systems is vital to determining the applicability of theoretical models. The influence of charge addition in these systems, via "doping" with K, is characterized by comparing pristine versus nitro-substituted OPE using photoelectron spectroscopies.

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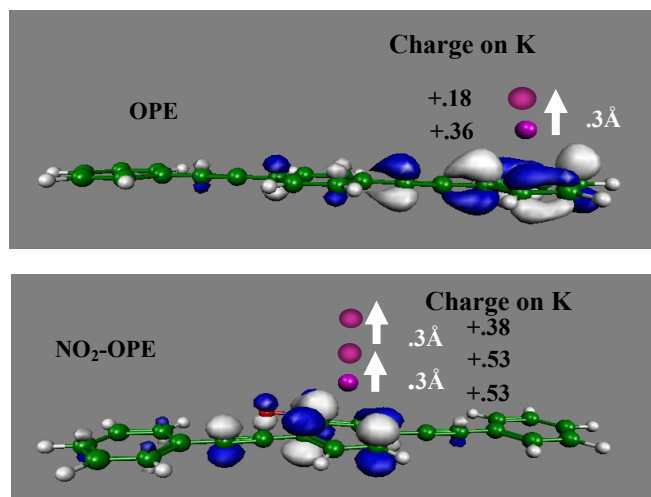
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Experimental measurements were performed to determine the impact of charge addition on the electronic structure of OPE oligomers using photoelectron spectroscopies. Sequential addition of K in unsubstituted OPE produces a gradual shift to higher binding energy, reminiscent of "rigid band" behavior, with relative shifts of π levels suggesting some distortion/conformation change. For a nitro-substituted oligomer, a markedly different behavior is observed with K addition. After an initial shift, the electronic levels are pinned for subsequent K addition before a final shift brings the spectrum to near coincidence with that for the pristine oligomer. Theoretical work is underway in an attempt to model this behavior and shed light on the differences that are brought about by -NO₂ substitutions. Preliminary results from theory are presented in the figures. Model calculations were performed to assess the relative degree of charge transfer from K atoms to OPE with and without -NO₂ substitution. Addition of the nitro group increases the amount of charge transferred as well as increasing the distance at which significant charge transfer occurs. These results seem to show hints of the experimental behavior where the nitro-substituted system exhibits larger spectral shifts (charge transfer) at lower concentrations (larger average distance from K to the molecule). These results are, however, very preliminary and much more work is needed. We are also investigating differences in the reorganization energy that accompanies charge addition/removal in these systems employing a combination of high-resolution gas phase photoelectron spectroscopy, in collaboration with researchers at the University of Arizona, and optical spectroscopy, again aided by theoretical calculation.

Impact:

The single most referenced result that spurred the interest in molecular electronics over the past ≈ 5 years was the report of negative differential resistance (NDR) behavior in nanoscale junctions contained the nitro-substituted molecule. To date, however, there are still many questions concerning the interpretation of these and similar experimental results. A number of potential explanations have been put forward, but little additional work has been performed to attempt to verify/discredit models. The work herein examines the differences that occur due to charge transfer to OPE (no NDR) versus nitro-substituted OPE (NDR observed) to determine first if significant differences exist and second to try to understand the origin of any variation in behavior. The measurements of relaxation energy will directly provide numbers for comparison to polaron-based theories which can predict hysteresis and NDR behavior but require quite high relaxation energies.

Model Calculations Comparing Charge Transfer From K to OPE vs. NO₂-OPE



Future Work

Theoretical modeling will aid in providing interpretations of the observed experimental behavior and linking it to the potential for charge addition effects to provide explanations of transport results. Further calculations, such as those depicted in the figures, will be performed as well as direct calculation of relaxation energies in the OPE and NO₂-OPE molecules.